Resolution of Optically Active Tris(1, 10-phenanthroline)vanadium(II) Complex

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Resolution of the optically active complexes with easily oxidized metal ions such as vanadium(II) has never been reported. However inert gas atmosphere makes it possible to prepare and resolve them. Recently we succeeded in preparation and resolution of tris(1, 10-phenanthroline)vanadium(II) diperchlorate under the complete inert gas atmosphere.

This complex was obtained by the following procedure.(1) 0.001 mol vanadous solution prepared by electrolytic reduction of $VOSO_4$ was mixed with 0.003 mol 1, 10-phenanthroline (phen) and the mixed solution was stirred until it turned dark blue showing the formation of $[V(phen)_3]^{2+}$ ion. Then this solution was added the saturated solution of 1 g potassium antimonyl-*d*-tartrate as resolving agent. After the less soluble diastereomer was precipitated, the $(-)_{589}[V(phen)_3]^{2+}$ ion was precipitated as the perchlorate salt by the addition of ammonium perchlorate solution. The whole procedure was carried out in nitrogen gas. Solvent water was freed from oxygen by nitrogen bubbling. For the measurements of UV and visible absorption spectrum and circular dichroism (CD),[*1] vacuum distilled methanol was used.

The absorption spectrum and also the CD curve resemble to those of $[Fe(phen)_3](ClO_4)_2$.(2) The observed spectra are shown in Fig. 1. The observed absorption intensity in UV region of vanadium complex is almost the same magnitude as those of the corresponding iron and nickel complexes. The observed CD intensity in the same region of vanadium complex is rather lower than those of the iron complex and nickel one, while the CD intensity of the iron complex is comparable with that of the nickel one. The lower intensity of the vanadium complex might be interpreted as partial resolution. Any trial of the resolution of the vanadium complex could not get the corresponding values of the iron and nickel complexes, as far as potassium antimonyl-*d*-tartrate is used as resolving agent. Resolution using other resolving agents is being carried out. The CD curve of the less soluble diastereomer has not been obtained because of its insolubility.

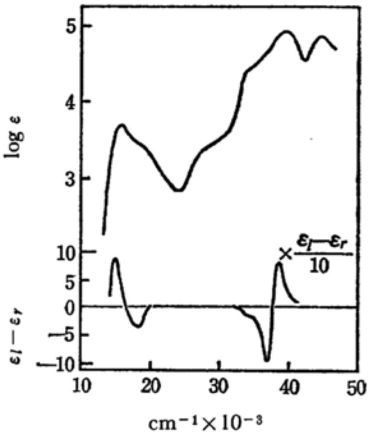

Fig. 1. Electronic absorption spectrum and CD curve of $(-)_{589}$-$[V(phen)_3](ClO_4)_2$.

The half-life of racemization assuming the first-order reaction is about 63 min in methanol at a room temperature. This value is as twice as that the iron complex and much less than that of the nickel complex.(3) When this complex was partially oxidized, the racemization became too fast to be measured.

Whole details will be published elsewhere.

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1) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **85**, 135 (1951).

[*1] Dr. T. Samejima kindly allowed us to use his CD instrument.

2) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1964).

3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y. (1958), p. 260.